Pulse-order invariance of the initial-state population in multistate chains driven by delayed laser pulses

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This paper shows that under certain symmetry conditions the probability of remaining in the initial state (the probability of no transition) in a chainwise-connected multistate system driven by two or more delayed laser pulses does not depend on the pulse order.

The process of stimulated Raman adiabatic passage (STIRAP) has received a great deal of attention in the past decade [1,2] because of its potential for efficient and robust population transfer between two states ψ_1 and ψ_3 via an intermediate state ψ_2. STIRAP uses two delayed laser pulses, a pump pulse $\Omega_P(t)$ linking states ψ_1 and ψ_2 and a Stokes pulse $\Omega_S(t)$ linking states ψ_2 and ψ_3. By applying the Stokes pulse before the pump pulse (counterintuitive order) and maintaining adiabatic-evolution conditions and two-photon resonance between states ψ_1 and ψ_3, one ensures complete and smooth transfer of population from ψ_1 to ψ_3, regardless of whether the intermediate state is on or off single-photon resonance. Applying the two pulses in the intuitive order [$\Omega_P(t)$ before $\Omega_S(t)$] leads to oscillations in the on-resonance case and to STIRAP-like transfer in the off-resonance case. The success of STIRAP has prompted its extension to multistate chainwise-connected systems [3–8], where a similar distinction between the intuitive and counterintuitive pulse orders exists.

In view of the great difference in the *final-state* population for the two pulse orders, surprisingly, the *initial-state* population has been found to be the same for both orders in the three-state case, provided the Hamiltonian has a certain symmetry [9]. The present paper extends this result to *multistate* chains. Thus it establishes another similarity between three-state and multistate systems.

The time evolutions of the probability amplitudes $\mathbf{c}(t) = [c_1(t), c_2(t), \ldots, c_N(t)]^T$ of the N states satisfy the Schrödinger equation (in units $\hbar = 1$) [10],

$$i\dot{\mathbf{c}}(t) = \mathbf{H}(t)\mathbf{c}(t). \tag{1}$$

In the rotating-wave approximation the Hamiltonian of the multistate chain is given by the tridiagonal matrix

$$\mathbf{H} = \begin{bmatrix} 0 & \Omega_{12} & 0 & \vdots & 0 & 0 \\ \Omega_{12} & \Delta_2 & \Omega_{23} & \vdots & 0 & 0 \\ 0 & \Omega_{23} & \Delta_3 & \vdots & 0 & 0 \\ \cdots & \cdots & \cdots & \ddots & \cdots & \cdots \\ 0 & 0 & 0 & \vdots & \Delta_{N-1} & \Omega_{N-1,N} \\ 0 & 0 & 0 & \vdots & \Omega_{N-1,N} & 0 \end{bmatrix}. \tag{2}$$

The system is supposed to have $N = 2n + 1$ states and the Rabi frequencies $\Omega_{j,j+1}(t)$ obey the relations

$$\Omega_{j,j+1}(t) = \begin{cases} \xi_j \Omega_P(t), & j \text{ odd}, \\ \xi_j \Omega_S(t), & j \text{ even}, \end{cases} \tag{3a}$$

$$\xi_j = \xi_{N+1-j}, \tag{3b}$$

$$\Omega_P(t) = \Omega_0 f(t - \tau), \tag{3c}$$

$$\Omega_S(t) = \Omega_0 f(t + \tau), \tag{3d}$$

and $f(-x) = f(x)$. The functions $\Omega_P(t)$ and $\Omega_S(t)$ describe the envelopes of the two pulses, 2τ is the pulse delay, Ω_0 is an appropriate unit of Rabi frequency, and the (constant) relative coupling strengths ξ_j are proportional to the corresponding Clebsch-Gordan coefficients. The detunings are supposed to obey the relations

$$\Delta_j(t) = \Delta_{N+1-j}(t), \tag{4a}$$

$$\Delta_j(t) = \Delta_j(-t), \qquad (j = 2, 3, \ldots, n+1). \tag{4b}$$

For example, Eqs. (3) and (4) apply to $2J + 1$-state systems (J integer), formed by the sublevels in $J \to J$ or $J \to J - 1$ transition, coupled by two laser pulses $\Omega_P(t)$ and $\Omega_S(t)$ with σ^+ and σ^- polarizations [4–6].

I shall show that when conditions (3) and (4) are satisfied the probability of remaining in the initial state (the probability of no transition) does not depend on the pulse order, i.e., it is invariant upon the interchange of $\Omega_P(t)$ and $\Omega_S(t)$. Since the $\Omega_P \rightleftarrows \Omega_S$ swap is equivalent to the index change $j \to N + 1 - j$ in $\mathbf{H}(t)$, the $\Omega_P \rightleftarrows \Omega_S$ invariance of the population of the initial state ψ_j is equivalent to the assertion that for a given pulse order, the probability of remaining in state ψ_j, provided the system is initially in state ψ_j, is equal to the probability of remaining in state ψ_{N+1-j}, provided the system is initially in state ψ_{N+1-j}. In terms of the transition matrix $\mathbf{U}(+\infty, -\infty)$, defined by $\mathbf{c}(+\infty) = \mathbf{U}(+\infty, -\infty)\mathbf{c}(-\infty)$, this invariance means that for any $j = 1, 2, \ldots, n + 1$,

$$U_{jj}(+\infty, -\infty) = U_{N+1-j,N+1-j}(+\infty, -\infty). \tag{5}$$

The proof of Eq. (5) is carried out in several steps. The first step is to show that the eigenvalues and the eigenstates of $\mathbf{H}(t)$ have certain symmetric properties. These properties lead to symmetries of the Hamiltonian in the adiabatic basis, which determine certain symmetries of the adiabatic transition matrix, which in turn lead to the property (5) of the diabatic transition matrix.

It follows from Eqs. (3) and (4) that the $\Omega_P \rightleftarrows \Omega_S$ swap is equivalent to time reversal in $\mathbf{H}(t)$,

$$\Omega_P(t) \rightleftarrows \Omega_S(t) \qquad \text{is equivalent to} \qquad t \to -t. \quad (6)$$

Hence, since the $\Omega_P \rightleftarrows \Omega_S$ swap does not change the eigenvalues of the Hamiltonian, $\mathbf{H}(-t)$ has the same eigenvalues as $\mathbf{H}(t)$. The eigenvalues $\lambda_j(t)$ of $\mathbf{H}(t)$ are therefore even functions of time,

$$\lambda_j(-t) = \lambda_j(t), \qquad (j = 1, 2, \ldots, N). \quad (7)$$

Since $\mathbf{H}(t)$ is real and symmetric, its eigenvalues are real and its eigenstates can be chosen real too. The components of the eigenstates (the adiabatic states) $\mathbf{w}^j(t) = [w_1^j(t), w_2^j(t), \ldots, w_N^j(t)]^T$ are expressed in terms of $w_1(t)$ (for simplicity, the label j is omitted for the moment) as

$$\frac{w_2(t)}{w_1(t)} = \frac{\lambda(t)}{\xi_1 \Omega_P(t)} \equiv g_2(t),$$
$$\frac{w_3(t)}{w_1(t)} = \frac{\lambda(t)\,[\lambda(t) - \Delta_2(t)] - \xi_1^2 \Omega_P^2(t)}{\xi_1 \xi_2 \Omega_P(t) \Omega_S(t)} \equiv g_3(t),$$
$$\ldots,$$

and in terms of $w_N(t)$ as

$$\frac{w_{N-1}(t)}{w_N(t)} = \frac{\lambda(t)}{\xi_1 \Omega_S(t)} \equiv g_2(-t),$$
$$\frac{w_{N-2}(t)}{w_N(t)} = \frac{\lambda(t)\,[\lambda(t) - \Delta_2(t)] - \xi_1^2 \Omega_S^2(t)}{\xi_1 \xi_2 \Omega_P(t) \Omega_S(t)} \equiv g_3(-t),$$
$$\ldots$$

Generally, one can write $w_k(t)/w_1(t) = g_k(t)$ and $w_{N+1-k}(t)/w_N(t) = g_k(-t)$. For $k = n+1$, one finds $g_{n+1}(-t) w_N(t) = g_{n+1}(t) w_1(t)$. It follows that

$$\frac{w_{N+1-k}(t)}{w_k(t)} = \frac{g_k(-t)}{g_k(t)} \frac{g_{n+1}(t)}{g_{n+1}(-t)},$$

for any $k = 1, 2, \ldots, n+1$. Hence

$$\begin{aligned} w_1(t) &= g_{n+1}(-t)/\nu(t), \\ w_2(t) &= g_2(t) g_{n+1}(-t)/\nu(t), \\ &\cdots, \\ w_{n+1}(t) &= g_{n+1}(t) g_{n+1}(-t)/\nu(t), \\ &\cdots, \\ w_{N-1}(t) &= g_{n+1}(t) g_2(-t)/\nu(t), \\ w_N(t) &= g_{n+1}(t)/\nu(t). \end{aligned} \quad (8)$$

The normalization factor $\nu(t)$ is obviously invariant upon time reversal, which means that $\nu(-t) = \nu(t)$. Equations (8), which are valid for $g_{n+1}^j(t) \neq 0$ (case I), lead to the relation (with the label j restored)

$$w_k^j(-t) = w_{N+1-k}^j(t), \qquad \text{(case I)}, \quad (9a)$$

with $k = 1, 2, \ldots, n+1$.

If $g_{n+1}^m(t) = 0$ (case II) for a certain $\lambda_m(t)$, we have $w_{n+1}^m(t) = 0$ and $w_{n+2}^m(-t) = -w_n^m(t)$, which leads to

$$w_k^m(-t) = -w_{N+1-k}^m(t), \qquad \text{(case II)}, \quad (9b)$$

with $k = 1, 2, \ldots, n+1$. Such a case arises for the zero-eigenvalue eigenstate in systems with $N = 3, 7, 11, \ldots$ states and zero detunings.

The symmetry relations (9) for the adiabatic states determine certain symmetries of the Hamiltonian in the adiabatic basis. The transformation from the original (diabatic) basis to the adiabatic basis, $\mathbf{c}(t) = \mathbf{W}(t)\mathbf{a}(t)$, is carried out by the orthogonal matrix $\mathbf{W}(t)$, whose columns are the normalized eigenvectors $\mathbf{w}^j(t)$. Here $\mathbf{a}(t) = [a_1(t), a_2(t), \ldots, a_N(t)]^T$ is the column-vector of the adiabatic probability amplitudes. The Schrödinger equation in the adiabatic basis reads

$$i\dot{\mathbf{a}}(t) = \mathbf{H}^a(t)\mathbf{a}(t), \quad (10)$$

where $\mathbf{H}^a(t) = \mathbf{H}^{\rm adb}(t) + \mathbf{H}^{\rm nonadb}(t)$ with

$$\mathbf{H}^{\rm adb}(t) = \mathbf{W}^T(t)\mathbf{H}(t)\mathbf{W}(t), \quad (11a)$$
$$\mathbf{H}^{\rm nonadb}(t) = -i\mathbf{W}^T(t)\dot{\mathbf{W}}(t). \quad (11b)$$

The adiabatic part $\mathbf{H}^{\rm adb}(t)$ is a diagonal matrix containing the eigenvalues $\lambda_j(t)$ of $\mathbf{H}(t)$ on the main diagonal. The nonadiabatic part $\mathbf{H}^{\rm nonadb}(t)$ has zeros on the main diagonal, while the off-diagonal elements are equal to the nonadiabatic couplings $H_{jk}^{\rm nonadb}(t) = -i\mathbf{w}^j(t) \cdot \dot{\mathbf{w}}^k(t)$. It is readily seen from Eq. (9a) that the nonadiabatic coupling between two case-I adiabatic states $\mathbf{w}^j(t)$ and $\mathbf{w}^k(t)$ is an odd function of time. Really,

$$\begin{aligned} H_{jk}^{\rm nonadb}(-t) &= i\sum_{l=1}^{N} w_l^j(-t)\dot{w}_l^k(-t) \\ &= i\sum_{l=1}^{N} w_{N+1-l}^j(t)\dot{w}_{N+1-l}^k(t) \\ &= -H_{jk}^{\rm nonadb}(t), \quad \text{(case I} \cdot \text{case I)}. \end{aligned} \quad (12a)$$

The nonadiabatic coupling between a case-I eigenstate $\mathbf{w}^j(t)$ and a case-II eigenstate $\mathbf{w}^m(t)$ is an even function,

$$H_{jm}^{\rm nonadb}(-t) = H_{jm}^{\rm nonadb}(t), \quad \text{(case I} \cdot \text{case II)}. \quad (12b)$$

The symmetry of $\mathbf{H}^a(t)$ determines a certain symmetry of the adiabatic transition matrix $\mathbf{U}^a(+\infty, -\infty)$, defined as $\mathbf{a}(+\infty) = \mathbf{U}^a(+\infty, -\infty)\mathbf{a}(-\infty)$. In order to find it, I introduce the evolution matrix $\mathbf{G}(t, 0)$ via $\mathbf{a}(t) = \mathbf{G}(t, 0)\mathbf{a}(0)$. Evidently, the first column of $\mathbf{G}(t, 0)$ is the solution of Eq. (10) for the initial condition $\mathbf{a}(0) = (1, 0, 0, \ldots, 0)^T$, the second column is the solution for $\mathbf{a}(0) = (0, 1, 0, \ldots, 0)^T$, and so on. When all nonadiabatic couplings are odd functions of time [Eq. (12a)], time reversal in Eq. (10) is equivalent to complex conjugation of $\mathbf{a}(t)$ (case A). When a case-II eigenstate $\mathbf{w}^m(t)$ exists [then the nonadiabatic couplings involving it are even functions, Eq. (12b)], time reversal in Eq. (10) is equivalent to complex conjugation of $\mathbf{a}(t)$ and change of sign of $a_m(t)$ (case B). This means that

$$\mathbf{G}(-t,0) = \begin{cases} \mathbf{G}^*(t,0), & \text{(case A)}, \\ \mathbf{IG}^*(t,0)\mathbf{I}, & \text{(case B)}, \end{cases} \tag{13}$$

where $\mathbf{I}$ is a diagonal matrix with units on its diagonal, except the (m,m)-th element which is -1. It follows from Eq. (13) and the unitarity of $\mathbf{G}$ that

$$\begin{aligned} \mathbf{U}^a(+\infty,-\infty) &= \mathbf{G}(+\infty,0)\mathbf{G}(0,-\infty) \\ &= \mathbf{G}(+\infty,0)\mathbf{G}^\dagger(-\infty,0) \\ &= \begin{cases} \mathbf{G}(+\infty,0)\mathbf{G}^T(+\infty,0), & \text{(case A)}, \\ \mathbf{G}(+\infty,0)\mathbf{IG}^T(+\infty,0)\mathbf{I}, & \text{(case B)}. \end{cases} \end{aligned}$$

Hence

$$[\mathbf{U}^a(+\infty,-\infty)]^T = \begin{cases} \mathbf{U}^a(+\infty,-\infty), & \text{(case A)}, \\ \mathbf{IU}^a(+\infty,-\infty)\mathbf{I}, & \text{(case B)}. \end{cases} \tag{14}$$

The transition matrices in the diabatic and adiabatic bases are related by

$$\mathbf{U}(+\infty,-\infty) = \mathbf{W}(+\infty)\mathbf{U}^a(+\infty,-\infty)\mathbf{W}^T(-\infty).$$

Then one finds from Eqs. (9) and (14) that in both cases A and B,

$$\begin{aligned} &U_{N+1-j,N+1-j}(+\infty,-\infty) \\ &\quad = \sum_{k,l=1}^{N} w^k_{N+1-j}(+\infty)U^a_{kl}(+\infty,-\infty)w^l_{N+1-j}(-\infty) \\ &\quad = \sum_{k,l=1}^{N} w^k_j(-\infty)U^a_{lk}(+\infty,-\infty)w^l_j(+\infty) \\ &\quad = U_{jj}(+\infty,-\infty). \end{aligned}$$

This completes the proof.

It should be emphasized that the pulse-order invariance applies to the population of the initial state only, while the populations of all other states depend on the pulse order. This is clearly demonstrated in Fig. 1 where the initial-state population P_1 and the final-state population P_5 are plotted against the pulse delay τ in the case of a five-state system, initially in state ψ_1. The figure shows that P_5 behaves very similarly to STIRAP with a broad plateau of high transfer efficiency for $\tau > 0$ and oscillations for $\tau < 0$ [1,2,9]. In contrast, P_1 is a symmetric function of τ, as follows from the above results.

Finally, the pulse-order invariance of the initial-state population has been derived without the assumption of adiabatic evolution. Hence it applies to the general nonadiabatic case, as long as the pulse duration is long enough to validate the rotating-wave approximation.

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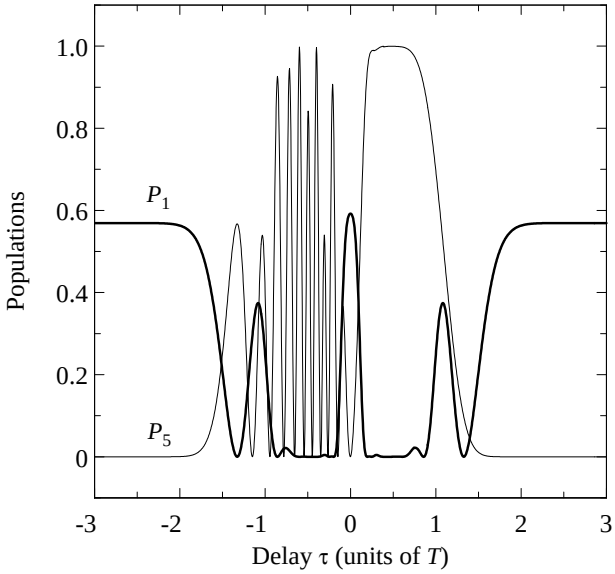

FIG. 1. The initial-state population P_1 and the final-state population P_5 for a five-state system, initially in state ψ_1, plotted against the pulse delay τ in the resonance case ($\Delta_2 = \Delta_3 = \Delta_4 = 0$). The Rabi frequencies of the two pulses are given by Eqs. (3) and have Gaussian shapes, $\Omega_P(t) = \Omega_0 \exp[-(t-\tau)^2/T^2]$ and $\Omega_S(t) = \Omega_0 \exp[-(t+\tau)^2/T^2]$, with $\xi_1 = \xi_4 = \sqrt{1/3}$, $\xi_2 = \xi_3 = \sqrt{1/2}$, and $\Omega_0 T = 30$.

[1] K. Bergmann and B. W. Shore, in *Molecular Dynamics and Spectroscopy by Stimulated Emission Pumping*, ed. H. L. Dai and R. W. Field (World Scientific, Singapore, 1995) and references therein.

[2] K. Bergmann, H. Theuer and B. W. Shore, Rev. Mod. Phys. **70**, 1003 (1998) and references therein.

[3] B. W. Shore, K. Bergmann, J. Oreg, and S. Rosenwaks, Phys. Rev A **44**, 7442 (1991).

[4] P. Pillet, C. Valentin, R.-L. Yuan, and J. Yu, Phys. Rev. A **48**, 845 (1993).

[5] L. Goldner, C. Gerz, R. Spreeuw, S. Rolston, C. Westbrook, W. Phillips, P. Marte and P. Zoller, Phys. Rev. Lett. **72**, 997 (1994).

[6] H. Theuer and K. Bergmann, Eur. Phys. J. **2**, 279 (1998).

[7] N. V. Vitanov, Phys. Rev. A **58**, 2295 (1998).

[8] N. V. Vitanov, B. W. Shore, and K. Bergmann, Eur. Phys. J. D **4**, 15 (1998) and references therein.

[9] N. V. Vitanov and S. Stenholm, Phys. Rev. A **55**, 648 (1997).

[10] B. W. Shore, *The Theory of Coherent Atomic Excitation* (Wiley, New York, 1990).